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Silicon Nanowires: Growth Studies Using Pulsed PECVD

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ABSTRACT

Silicon nanowires with high aspect ratios have been grown at high density using a variation of Plasma Enhanced Chemical Deposition (PECVD) known as Pulsed PECVD (PPECVD). Growth rate and morphology were investigated for a range of catalysts: gold, silver, aluminum, copper, indium and tin. The thickness of the catalyst layer was 100nm. Deposition was carried out in a parallel plate PECVD chamber at substrate temperatures up to 350°C, from undiluted semiconductor grade Silane. A 1 kHz square wave was used to modulate the 13.56 MHz RF power. Samples were analyzed using either a Phillips XL20 SEM or a ZEISS 1555 VP FESEM. The average diameter for nanowires grown using a gold catalyst layer was 150nm and the average length was 4µm although some nanowires were observed with lengths up to 20µm. Back-scattered-electron images clearly show gold present at the tips of the silicon nanowires grown using gold as a catalyst, confirming their growth by the vapor liquid solid (VLS) mechanism. Sporadic growth of nanowires was detected when using copper as a catalyst. Although gold performed best as catalyst for nanowire growth it was, however, closely followed by tin. The other catalysts produced nanowires with properties between these extremes.

INTRODUCTION

Silicon nanowires have potential uses in the semiconductor industry including possibly the next generation of photovoltaic solar cells. The most common method of fabrication involves the Chemical Vapor Deposition (CVD) of a gas containing silicon and the subsequent growth of silicon nanowires by the Vapor Liquid Solid (VLS) mechanism first proposed by Wagner and Ellis [1]. The presence of a metal catalyst droplet on one end of a nanowire is indicative of the VLS mechanism. Plasma Enhanced Chemical Vapor Deposition (PECVD) is a technique widely used in the production of amorphous and nanocrystalline silicon thin films. When used with substrates covered with a metal catalyst, PECVD has been used to produce silicon nanowires and is known to improve their deposition rate. [2]. A modification of PECVD is pulsed PECVD which uses a modulated plasma to aid the deposition process. We have previously shown [3] that PPECVD can be used to produce silicon nanowires with a greater area density than conventional PECVD. In the VLS mechanism the role of the catalyst is to encourage the growth of single crystal silicon nanowires. For silicon to be absorbed by the catalyst it needs to be highly soluble in the chosen metal. The choice of the metal catalyst is also known to affect the electrical properties of resulting nanowires [4].

A number of catalysts are commonly used in the growth of silicon nanowires. The most common is gold which does not form a silicide and has a bulk Au/Si eutectic temperature that is fairly low (363°C), this results in low temperature growth [2]. Gallium is another catalyst used mainly in the growth of bulk Si nanowires. The main advantage of using Gallium is the extremely low Ga/Si eutectic temperature (30°C) which should permit low temperature growth of silicon nanowires [5]. Titanium has been used to grow silicon nanowires; however a mechanism other than VLS is required to explain the growth of these nanowires as the growth temperature is well below the melting point of the catalyst. The advantage of Ti is that it does not form deep mid-gap levels and the solubility and diffusion coefficients of Ti are low in silicon [6]. Iron has been used to grow silicon based nanowires, however, the deposition method used involves physical evaporation or laser ablation of an Au/Fe target [7,8]. Cobalt has been used to grow silicon nanostructures via the VLS mechanism, the resulting growth described as a "flower" [9]. Zinc has also been used to grow nanowires via the VLS mechanism, the resulting nanowires were observed to have different electrical properties than those grown with a gold catalyst under the same conditions [4]. VLS growth of silicon whiskers has also been shown to occur for catalysts including Pt, Ag, Pd, Cu and Ni [1]. The aim of this work was to use as catalysts gold, tin, aluminum, indium, silver and copper with pulsed PECVD in an endeavor to improve the yield of silicon nanowires under the conditions imposed by the available equipment.

EXPERIMENT

Both glass and polished n-type Si (100) substrates were used for the deposition of silicon nanowires in this study. The substrates were cleaned in an ultrasonic bath in several steps using decon-90, ultra-pure water and propanol. After a final ultra-pure water rinse the substrates were dried using high purity nitrogen before being transferred into a vacuum system for deposition of the catalyst layer. The native oxide layer was left intact on the crystalline silicon substrates to ensure non-epitaxial growth. Catalyst layers with an average thickness of 100nm were deposited onto the substrates by thermal evaporation of high purity catalyst metal from a tungsten wire or boat under vacuum. The thickness of the catalyst layer was measured in-situ using a quartz crystal microbalance. Silicon nanowires were grown in a separate chamber using pulsed PECVD which has been previously shown to promote improved growth. The PECVD system has parallel plate electrodes and uses a 13.56 MHz RF signal to generate the plasma. The addition of square wave modulation at 1 kHz produces pulsed PECVD. The deposition was performed in 2.7 to 3.0 Torr of silane and at a substrate temperature of 335°C. Plasma duration ranged from 10 to 40 seconds. A control sample using gold as a catalyst was present during each deposition. The samples were analyzed using either a Philips XL20 SEM or ZEISS 1555 VP FESEM.

DISCUSSION

Each of the catalysts used produced nanowires, however, the results ranged from a high density of nanowires over a substantial area of the substrate to others where few nanostructures grew on localized regions of the substrate. The morphology of the nanowires grown as part of this study was found to be dependant on the catalyst that was used. Nanowires produced using Silver are shown in figure 1. They were found to have a range of diameters and lengths. These

nanowires exhibit some growth defects such as kinking but generally tended to grow as long straight wires. Present on the end of some of the nanowires is a bright tip that is similar in appearance to the droplet seen on gold nanowires grown by the VLS mechanism. Aluminum was a largely unproductive catalyst yet did produce some structures similar in appearance to the silver catalyzed nanowires shown in figure 1. They were much larger, however, having diameters up to ten times as large as nanowires grown by other catalysts. The diameters of the wire-like structures were fairly uniform and many exhibited a droplet at one end, indicative of VLS growth. Nanowires grown by using indium were similar in appearance to silver and aluminum. These also exhibited a range of diameters.

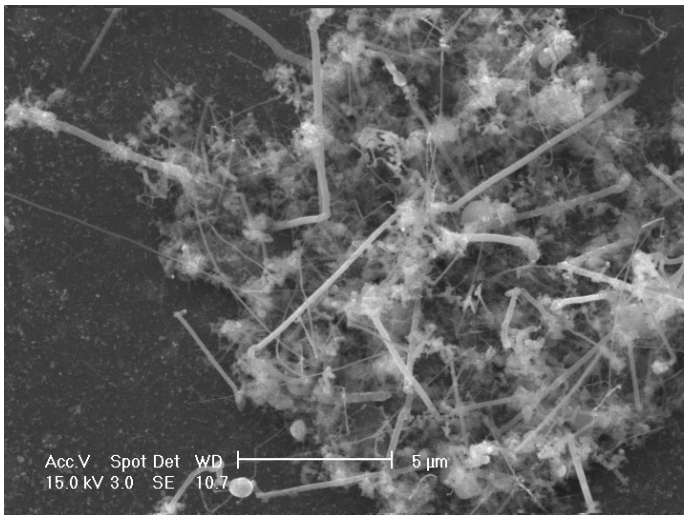


Figure 1. Silver-catalyzed nanowires growing out of more complex structures.

Nanowires grown using gold have largely uniform diameters as seen in figure 2.

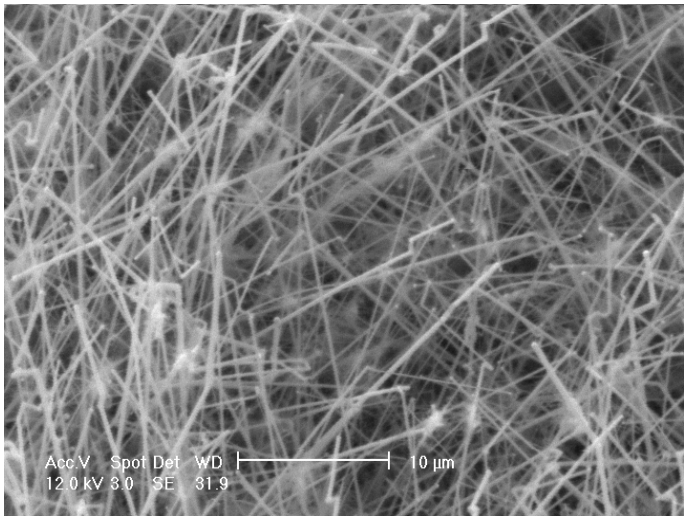


Figure 2. The appearance of a high density of Silicon nanowires grown using Au as a catalyst.

These show some growth defects such as kinking and commonly have a droplet visible on the tip of the nanowire. Although the nanowires are mainly straight and of high aspect ratio some curled or worm-like structure have also been observed. Nanowires grown using gold have a much higher growth density (NW/μm^2) than other catalysts. Using copper yielded very few nanowires under the growth conditions used. Copper mainly produced droplet-like structures on the surface of the substrate. Some of these may exhibit signs of growth. Scattered amongst these were the occasional nanowire, with largely uniform diameters and few growth defects. Indium produced very few nanowires under the growth conditions used. The nanowires had both crystalline like growth defects and amorphous worm-like structures, often in the same wire. A bright tip was visible on the end of a number of the nanowires. Tin produced a high density of very fine, uniform and long nanowires which are ribbon like in appearance as can be seen in figure 3. These nanowires have few growth defects and tend to bend rather than kink. Their sinuous form is in contrast to the ramrod straightness of nanowires initiated by the other catalysts.

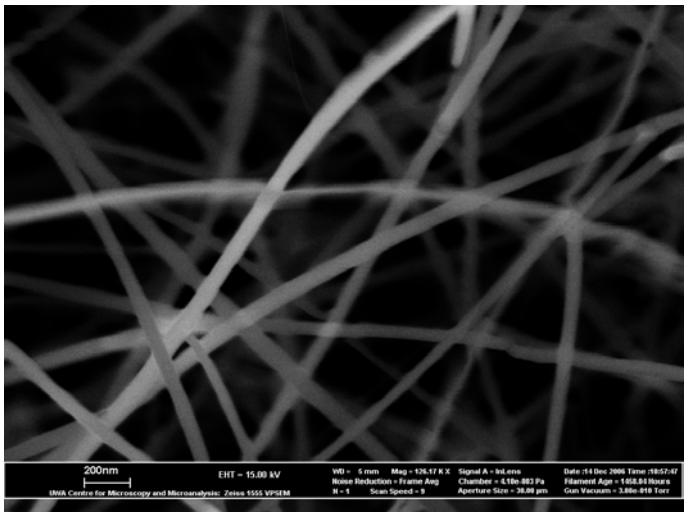
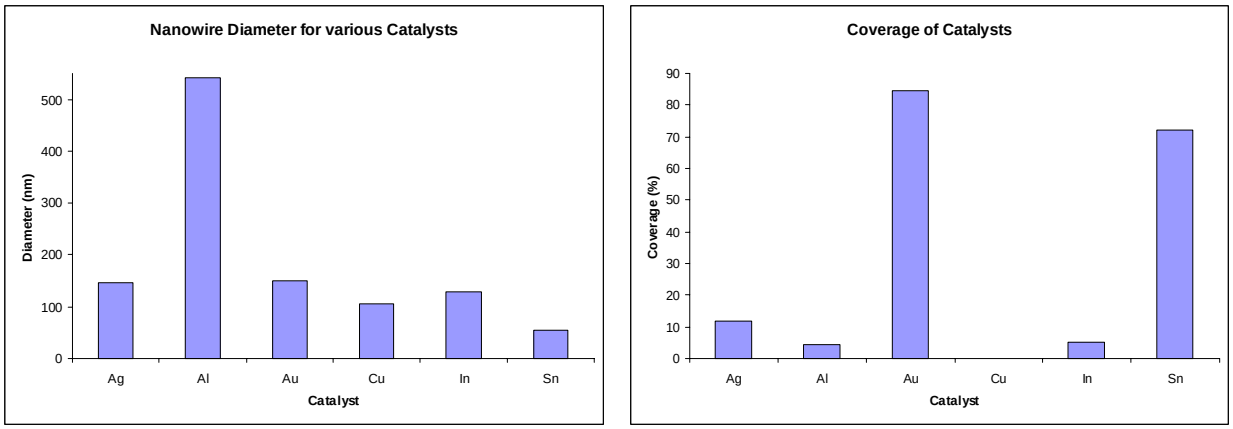


Figure 3. Long ribbon like nanowires grown using Sn as a catalyst.

The average diameters of the nanowires are compared in figure 4a. It can be seen from this plot that aluminum catalyzed wires have the greatest diameter, tin nanowires have the smallest and the other catalysts have very similar diameters. To compare how well the nanowires are produced by the different catalysts the “coverage” has been plotted in figure 4b. The coverage is expressed as a percentage of the sample covered by the nanowires. It can be seen that gold produces the greatest coverage of nanowires at 84.5% followed by tin at 72.3%. The other catalysts have coverage below 12% indicating that tin and gold produce a greater density of nanowires for the growth conditions used.

The physical properties of the catalyst used to grow the silicon nanowires are likely to have an impact on the growth and morphology of the silicon nanowires. For example the melting point, or eutectic point of Au and Si determine the minimum temperature required for the growth of silicon nanowires via the VLS mechanism.



(a) **(b)**

Figure 4. **(a)** Nanowire diameters for various catalysts.
(b) The coverage of nanowires for various catalysts.

The melting and eutectic points of the various catalysts used in this study are listed in table I.

Table I. Melting points and eutectic points of the six catalysts used in this study [2, 10, 11, 12]

Catalyst	Melting Point	Si Eutectic Point
	°C	°C
Ag	961.78	845
Al	660.32	577
Au	1064.18	363
Cu	1084.62	802
In	156.6	156.63
Sn	231.93	231.9

The nanowires grown using gold as the catalyst have shown the gold tip on the nanowires that is indicative of the VLS growth mechanism. This confirms that the VLS mechanism applies to the growth of silicon nanowires using PPECVD. The VLS mechanism is the most probable growth mechanism for the nanowires catalyzed by a thin film of tin, as the deposition temperature was above the melting point of tin. The diameter of the nanowires produced in this study was on average 54nm. The long nanowires curve gently and are loosely bound and appear to be ribbon like. There are very few kinks or growth defects that would indicate crystallinity. They may be amorphous but this has not been confirmed. It was found in this study that the use of both silver and copper as catalysts produced silicon nanowires. The silver catalyzed nanowires often showed a bright tip under examination by the SEM which indicates the VLS mechanism is responsible for the growth. The Cu catalyzed nanowires did not show any droplets on the end of the nanowires. This may be the result of either the catalyst being consumed by the silicon nanowire to the point where the diameter and composition of the tip is indeterminate from the bulk, or a different nanowire growth mechanism. The higher temperature of the eutectic points of

Al-Si, Ag-Si and Cu-Si provides an explanation as to why the growth using these catalysts was so ineffective. The substrate temperature employed in this study was too low for the VLS mechanism to be operative, resulting in sporadic growth due to some other mechanism.

CONCLUSIONS

Silicon nanowires have been grown by PPECVD using Ag, Al, Au, Cu, In and Sn as catalysts. It was found that gold was the most effective catalysts from this group at the growth temperatures and conditions used producing nanowires with substrate coverage of seven to eight times greater than the other catalysts. Tin was almost as effective and produced nanowires with an average diameter less than the other catalysts. The tin-catalyzed nanowires showed a morphology which appeared to possibly be amorphous. For high density growth of silicon nanowires at ~340°C via pulsed PECVD tin and gold are the preferred catalysts.

ACKNOWLEDGMENTS

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